

Article

Infiltration of CsPbI₃:EuI₂ Perovskites into TiO₂ Spongy Layers Deposited by gig-lox Sputtering Processes

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Abstract: Perovskite solar cells have become a popular alternative to traditional silicon solar cells due to their potential to provide high-efficiency, low-cost, and lightweight solar energy harvesting solutions. However, the multilayer architecture of perovskite solar cells demands careful investigation of the interaction and interfacing between the various layers, as they play a crucial role in determining the overall performance of the cell. In this context, the present work aims at analyzing the coupling between a spongy transparent electron-transporting layer (ETL) and perovskite in a formulation CsPbI₃:EuI₂. The ETL used in this work is a transparent mesoporous TiO₂ layer called “gig-lox” (grazing incidence angle geometry–local oxidation), which has been optimized to boost the interfacing with the perovskite for achieving a highly interconnected blend of materials. The gig-lox TiO₂ ETL shows a high surface wettability with respect to the perovskite solution, especially after pre-annealing at 500 °C, and this enables the perovskite material to deeply infiltrate throughout it. The surface wettability of the gig-lox TiO₂ has been estimated by contact angle measurements, while the deep infiltration of the perovskite material has been demonstrated through X-ray diffraction and transmission electron microscopy analyses. Thanks to the achieved deep infiltration, the photo-generated charge injection from the perovskite into the mesoporous oxide is enhanced with respect to the use of a planar compact oxide, as shown by the photoluminescence measurements. The mainstay of the approach resides in the ETL that is deposited by a solvent-free sputtering method and is up-scalable for high industrial throughput.



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1. Introduction

The increasing global demand for energy calls for a shift towards renewable energy sources, and photovoltaics is at the forefront of this transition [1]. As the world’s population continues to grow, the demand for energy is expected to increase significantly [2]. Therefore, it is crucial to phase out fossil fuels and transition towards sustainable and renewable energy sources to meet this demand. In this context, perovskite solar cells (PSCs) have emerged as a promising alternative to traditional silicon solar cells (SSCs) [3,4].

One of the main advantages of PSCs is their potential for high efficiency in converting sunlight into electricity. Perovskite materials possess unique electronic and optical properties that allow for efficient energy conversion. In fact, PSCs have already demonstrated efficiencies greater than 25%, which is comparable to the record efficiency of SSCs [5,6]. This high efficiency, coupled with their low manufacturing cost, makes PSCs an attractive

option for large-scale deployment. Manufacturing PSCs is much cheaper than manufacturing SSCs, as they can be fabricated using simple low-cost techniques. This affordability factor can play a significant role in democratizing access to solar energy for people living in remote or underprivileged areas. Moreover, PSCs can be used in various applications, including flexible and lightweight devices such as wearables, which is not feasible with SSCs [7].

Despite their significant advantages, PSCs still face several challenges, including stability and durability issues, that need to be solved for their commercialization. The stability issue is a major concern in PSCs due to their sensitivity to moisture, heat, and light. However, significant progress has been made in recent years to address these challenges, and there is ongoing research to develop more stable and durable PSCs [8].

Titanium dioxide (TiO_2) is a pivotal component in PSCs acting as the ETL [9] in the device architecture (Figure 1).

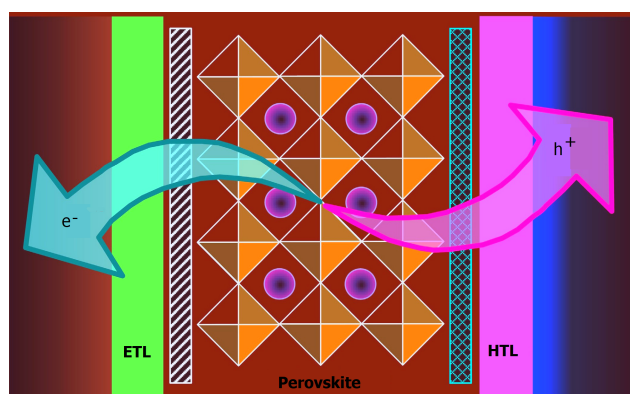


Figure 1. Simplified scheme for a typical structure of a perovskite solar cell.

The ETL is responsible for collecting the electrons generated by the perovskite layer upon exposure to light and transporting them to the external circuit [10]. TiO_2 is chosen as an ideal material as ETL in PSCs because of its high electron mobility, stability, and transparency in the visible region of the electromagnetic spectrum. TiO_2 can be also tailored with a large surface area, which is beneficial for the deposition of the perovskite layer and the formation of efficiently working contacts between the layers. The different TiO_2 morphologies, such as in the array of nanoparticles or in mesoporous structures, can be largely changed to optimize electron transport and overall PSCs performance [11]. In this context, we report a study featuring a special sponge of TiO_2 , called “gig-lox”, to infiltrate a $\text{CsPbI}_3\text{:EuI}_2$ perovskite. The study aims to improve the structural interconnection of the oxide with the perovskite layer and, indeed, the structural coupling between the two materials.

The method used to prepare the spongy gig-lox TiO_2 layer is safeguarded by a patent (US Patent 10,871,462), highlighting its novelty and uniqueness in the field. What sets this technique apart is its distinctive characteristic of producing the material through a sputtering physical method, ensuring a clean and environmentally friendly process. By adopting a physical production approach, we eliminate the reliance on chemical processes that may introduce pollutants or contaminants into the material [12].

The commitment to environmentally friendly production processes has become increasingly important in today’s world, where the focus on sustainability and reducing our ecological footprint is paramount. By utilizing this patented solvent-free technique for sustainable material production, we not only contribute to the development of advanced materials but also prioritize the well-being of our environment. Furthermore, the clean and non-polluting nature of this production method carries additional advantages. It enhances the safety of the manufacturing process, reducing potential risks associated with hazardous chemical reactions and minimizing the need for stringent safety measures. This aspect,

together with the high production throughput inherent in the sputtering process used to grow mesoporous gig-lox TiO_2 layers, is particularly valuable in industrial settings.

2. Materials and Methods

2.1. TiO_2 Deposition

The growth of spongy TiO_2 layers was achieved using a method called gig-lox. This technique involved depositing titanium species onto a substrate through grazing incidence sputtering from a metallic source. Simultaneously, the generated species underwent progressive local oxidation at the growing front. Our group previously discussed this technique in reference [13], and we have further enhanced it by optimizing the angular configuration to increase the porosity of the layers.

There are several advantages to this approach. Firstly, it enables a high deposition rate of 4 nm/min by establishing a metallic plasma at the source side, which prevents charging effects caused by surface oxidation. Secondly, it promotes the progressive local oxidation of the deposited species at the anode side. Lastly, the inclined (off-axis) titanium flux creates a shadowing effect from the starting seeds, resulting in additional meso-porosity in the material, in addition to the nano-porosity obtained from Thornton's approach. Importantly, the overall porosity is maintained even during post-deposition thermal treatments, for layer thicknesses up to 1000 nm, as described in the study by Alberti et al. [14]. In Figure 2, the experimental setup of the sputter was used.

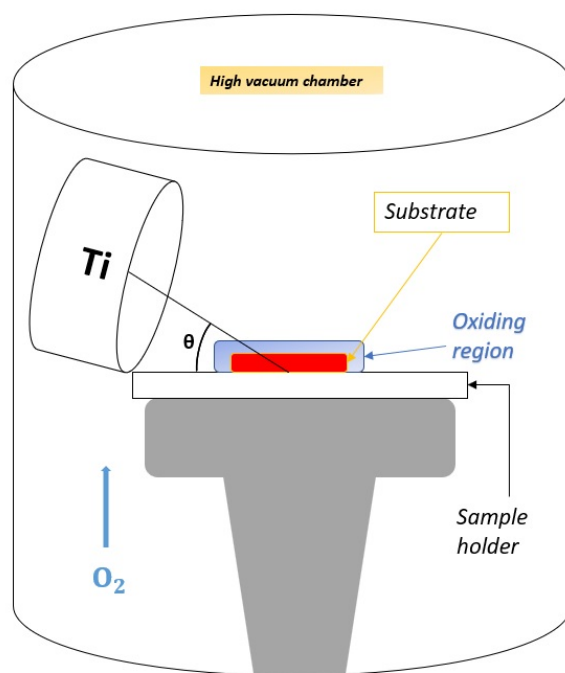


Figure 2. Experimental setup of the sputter for gig-lox TiO_2 deposition.

For our research, we used a 490 nm TiO_2 film, a typical value for the mesoporous layer in PSCs [15].

2.2. Perovskite Film Fabrication

To prepare a perovskite solution, we combined 1 M PbI_2 from Tokyo Chemical Industry and 1 M CsI from Tokyo Chemical Industry in a mixed solvent of DMF and DMSO in a 3:1 volume-to-volume ratio. We also prepared a solution of EuI_2 coating from Sigma-Aldrich (Taufkirchen, Germany) at a concentration of 0.1 M using the same mixed solvent. Both solutions were stirred at room temperature for 1 h. For $\text{CsPbI}_3:\text{EuI}_2$ samples, 1 mL of the PbI_2/CsI solution was then mixed with 0.5 mL of the EuI_2 solution to achieve the

desired stoichiometry. The resulting mixtures were further stirred for an hour. Throughout the entire process, the ambient air had a relative humidity of approximately 35%.

To deposit the perovskite films, we used a spin-coating method in an N_2 environment on a gig-lox TiO_2 substrate. The deposition process consisted of two steps: first, spinning at 1000 rpm for 10 s, followed by spinning at 5000 rpm for 25 s. Figure 3 illustrates the procedure.

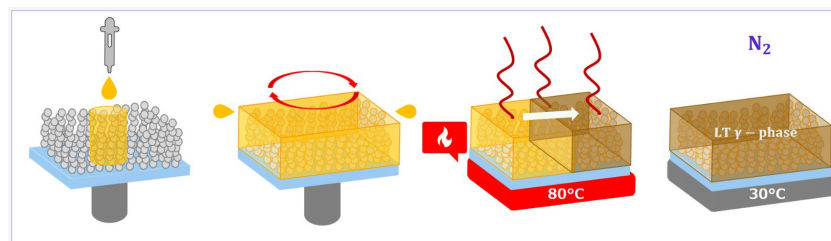


Figure 3. Representation of the procedure used for the $CsPbI_3:EuI_2$ deposition on gig-lox TiO_2 .

2.3. TiO_2 Samples Characterization

2.3.1. Micro-Raman Analysis

At room temperature, we performed micro-Raman measurements using a Horiba XploRA spectrometer that was equipped with a confocal microscope and a Peltier-cooled charge-coupled detector (CCD). A diode laser beam (excitation line @ 532 nm) was focused with a 50 μm spot on the sample's surface, with a power of about 1.5 W. The integration time for each measurement was 80 s with an accumulation time of 3 s.

2.3.2. Contact Angle Analysis

The homemade experimental setup depicted in Figure 4 was used to perform contact angle measurements. The setup is equipped with a LED lamp (580 lumens at 6500 K), a USB uEye camera (model UI-146xLE-C with a 1/2" CMOS sensor), and a convex lens (focal length of 16 mm and a maximum relative aperture of 1:1.4). A small drop (2 microliters) of perovskite solution $CsPbI_3:EuI_2$ (where a mixture of DMF and DMSO was used as solvent) was carefully placed onto the sample surface using a micrometer-controlled micro-syringe. The small volume of the drop (about one-fifth of the water capillary length [16]) and the short distance between the needle tip and the stage (less than 1 cm) allows for disregarding the effect of gravity [17]. Additionally, a waiting period of 3 days was used after the sample annealing to prevent temperature impacts on the drop's spread [18]. A high-definition camera positioned at the same level as the sample was employed to capture the drop image. As an example, Figure 4b,c shows the image of water drops on the two investigated gig-lox TiO_2 layers. A custom MATLAB[®] script was then used to determine the contact angle value.

2.3.3. Transmission Electron Microscopy Analysis

Transmission electron microscopy (TEM) images were acquired using a probe-corrected Jeol ARM200 equipped with a JEOL 100 mm² energy-dispersive X-ray (EDX) detector. Images are acquired in scanning mode, using a 50 mrad high-angle annular dark field (HAADF) detector. EDX spectra are acquired in spectrum image configuration scanning all over the film thickness, from the surface to the bottom interface. Any attempt to prepare TEM samples using water results in a perovskite material dissolution even inside the porous structure. To avoid any modification in the perovskite material the TiO_2 film was scratched away from the glass substrate directly on a TEM carbon grid.

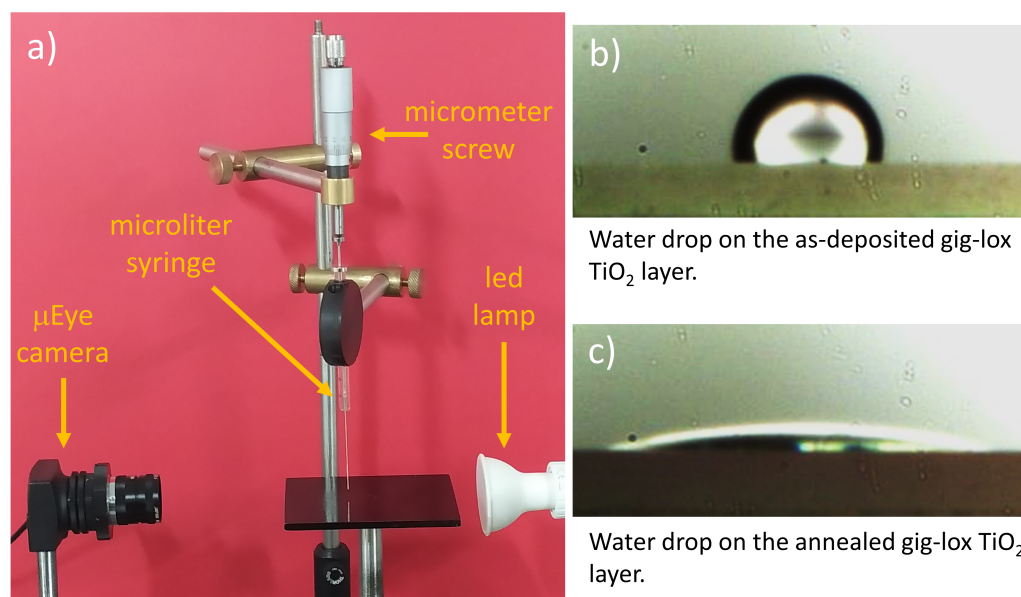


Figure 4. (a) Photo of the used contact angle setup. (b,c) Water drop images on the investigated gig-lox TiO₂ layers.

2.3.4. X-ray Diffraction Analysis

For X-ray diffraction (XRD) analyses, we used a D8-Discover Bruker AXS diffractometer. The instrument was equipped with a Cu-Kα source, a Goebel mirror, axial Soller slits at the primary beam, and long Soller slits, and a detector at the secondary path.

2.3.5. Spectroscopic Ellipsometry Analysis

Data were collected for Spectroscopic Ellipsometry (SE) using a J.A. Woollam VASE equipment. In order to get both ellipsometric and transmittance data at the same time for transparent samples, the measurements were conducted in a vertical configuration. In the current study, transmittance measurements were taken in steps of 10 nm from 190 to 2500 nm [19–21].

2.3.6. Photoluminescence Spectroscopy Analysis

Photoluminescence measurements play a crucial role in elucidating the optical properties and behavior of the studied materials. To conduct accurate and reliable photoluminescence measurements, we used a custom-built experimental apparatus, as depicted in Figure 5. This bespoke setup was specifically designed to capture and analyze the emitted light from the samples under investigation.

A 380 nm to 465 nm wavelength LED [22] illuminates the sample placed 1 cm away under the beam. A light conveyor allows light to pass up to the detector (Hamamatsu C12880MA [23]) with a well-defined area of 0.785 square centimeters. The data collected in this way is sent to an ARDUINO® board which allows them to be analyzed on the PC using dedicated software. The entire apparatus is placed inside a box with black walls in order to isolate the system from ambient light noise.

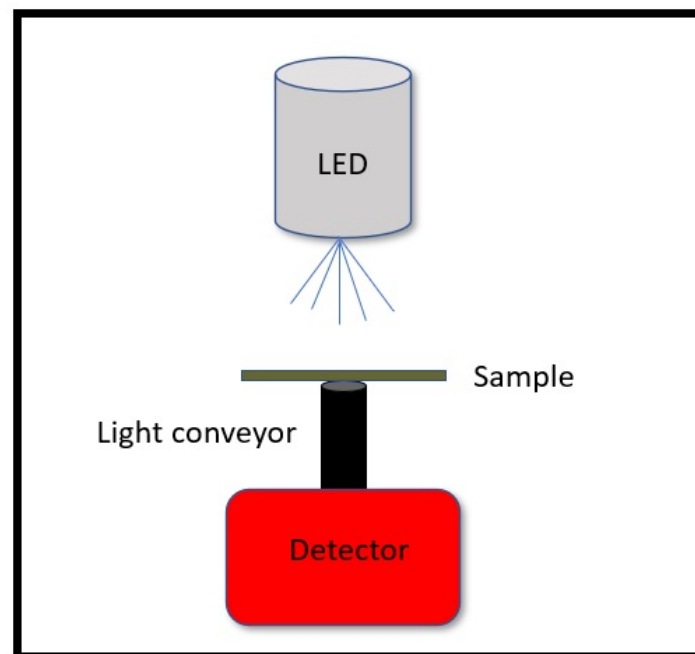


Figure 5. Scheme of the experimental apparatus used for photoluminescence measurements. At the top is the 380 nm to 465 nm wavelength LED. The light passing through the sample is directed to the detector.

3. Results and Discussion

3.1. Micro-Raman Results

The samples' microstructural investigation was first carried out by micro-Raman analyses to give information about the TiO_2 phases. Figure 6 displays Raman spectra for the 400 nm thick gig-lox TiO_2 layers before and after thermal treatment at 500 °C for 30 min in air environment [24,25]. The Raman features observed in the as-deposited sample are typical of the TiO_2 anatase/rutile mixture [26,27]. Following the thermal treatment at 500 °C, the Raman peaks assigned to B_{1g} , A_{1g} , and E_g vibrational modes of TiO_2 anatase phase are more defined [28].

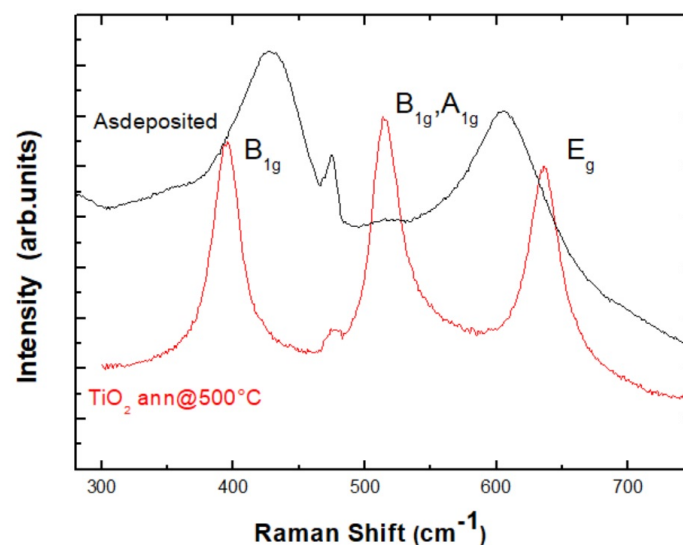


Figure 6. Micro-Raman spectra of TiO_2 before and after annealing at 500 °C.

It is expected that our anatase film exhibits a high degree of hydrophilicity [29]. Thus, the impact of the physicochemical properties of the material on wettability has been examined, and the results are reported in the next section.

3.2. Contact Angle Results

The contact angle is a measure of the wettability of material, therefore indicating the ability of water or other liquids to infiltrate or to be absorbed by the surface [30,31]. We have measured the contact angle of the TiO_2 gig-lox samples. Figure 7 shows the drops of $\text{CsPbI}_3:\text{EuI}_2$ perovskite solution diluted in the DMF and DMSO solvent formed on the surface of the as-deposited (a) and annealed (b) TiO_2 gig-lox layers. The measured contact angles (CAs) are 53.6° and 6.1° , respectively. The first value indicates that the as-deposited film has a relatively good degree of wettability, while the second CA value corresponds to a super-hydrophilic surface [32], indicating that the thermally treated TiO_2 sample exhibits an improved wettability [33] towards the $\text{CsPbI}_3:\text{EuI}_2$ solution. It is worth mentioning that the contact angle value of the same solution on a bare glass is 39.6° .

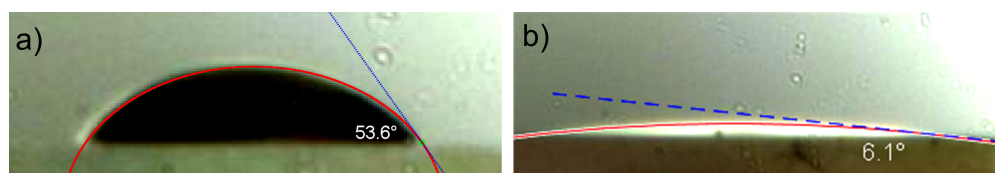


Figure 7. Contact angle images for droplets of perovskite solutions on (a) as-deposited and (b) annealed TiO_2 samples, respectively.

The achievement of enhanced wettability in the annealed sample represents a significant breakthrough in the development of perovskite solar cells. This improvement can be attributed to the heightened interaction between the ETL and the photoactive layer, a crucial aspect that we have extensively investigated to shed light on the underlying mechanisms [34].

By employing state-of-the-art (TEM) analyses, we delved deep into the intricate interplay between the ETL and the photoactive layer. These analyses provided us with invaluable insights into the structural and compositional changes occurring at the interface, unraveling the mechanisms responsible for the observed improvement in wettability.

3.3. Transmission Electron Microscopy Results

The fine structure of the gig-lox layer, for instance, can significantly affect its compatibility with the perovskite layer and, ultimately, the overall efficiency of the solar cell. Therefore, it is critical to have a comprehensive understanding of the structure of both the gig-lox layer and the perovskite material.

In this regard, the combination of transmission electron microscopy and scanning transmission electron microscopy with energy-dispersive X-ray spectroscopy analyses is a powerful tool for investigating the structure and composition of materials at the nanoscale. TEM/STEM can provide high-resolution images of the materials' internal structure and morphology, while EDX can reveal the chemical composition of the materials.

In our study, we used TEM/STEM and EDX analyses to reveal the fine structure of the gig-lox layer and its infiltration capability with the $\text{CsPbI}_3:\text{EuI}_2$ perovskite material. The resulting images and spectroscopy data obtained through these analyses provided a comprehensive understanding of the materials' structure and composition, which was crucial in designing an efficient and compatible solar cell.

Figure 8 depicts a HAADF STEM image of the annealed sample and Figure 9 the related EDX spectrum. The bright contrast inside the porous areas of the TiO_2 discloses the presence of an extra-material with a higher molecular weight. EDX data allowed us to corroborate the presence of $\text{CsPbI}_3:\text{EuI}_2$ throughout the layer, from the topmost part to the bottom of the layer, showing the characteristic peaks of cesium, lead, and iodine, in addition to titanium and oxygen features.

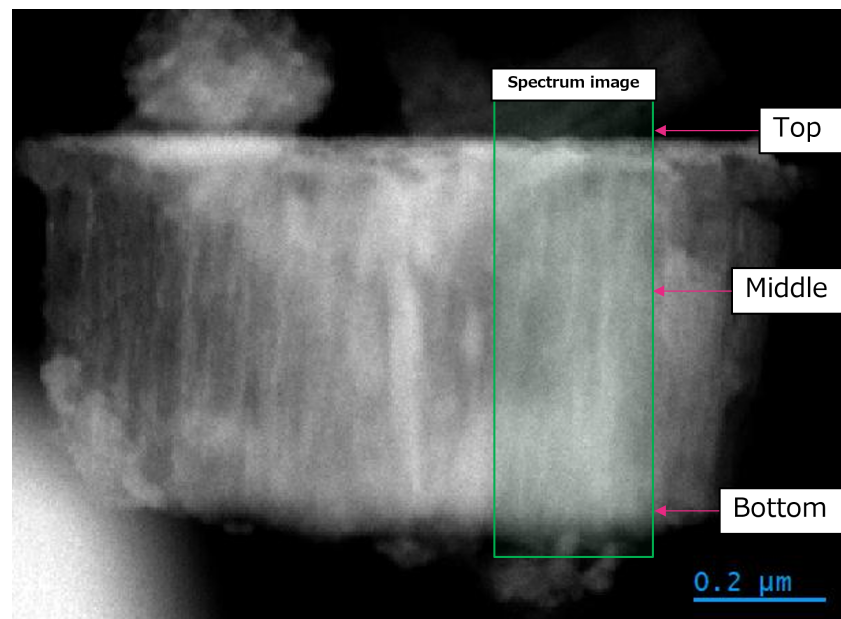


Figure 8. STEM analyses on the TiO_2 gig-lox layer after $\text{CsPbI}_3\text{:EuI}_2$ infiltration.

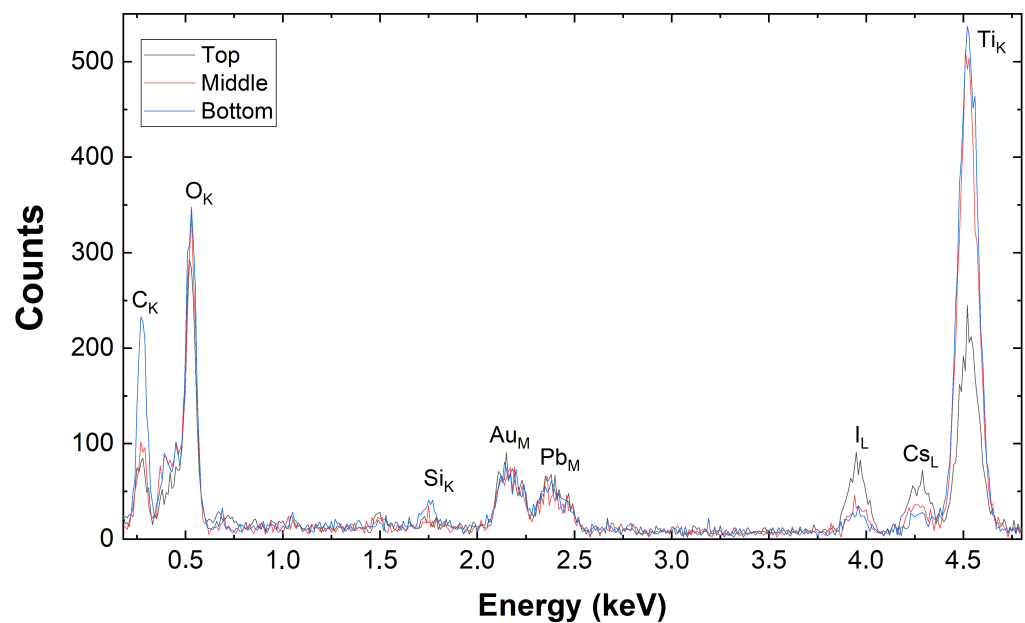


Figure 9. EDX spectra of the annealed TiO_2 gig-lox layer after $\text{CsPbI}_3\text{:EuI}_2$ infiltration.

In addition, we performed an EDX mapping image of the cross-sectional view (Figure 10).

In the same section of the sample, a clear demonstration of the seamless integration between the two materials is provided, as the pores are visibly filled with all the species present in the perovskite formulation. This serves as compelling evidence for the successful intermixing of the two materials.

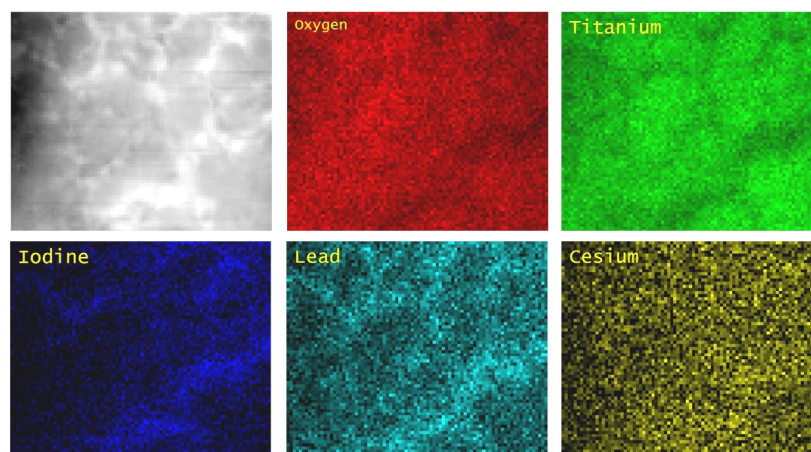


Figure 10. Cross-sectional view of the gig-lox TiO_2 -perovskite blend and the related chemical maps obtained by EDX. The TiO_2 pores are fully filled by the perovskite material as highlighted by the presence of all the species introduced in its formulation.

3.4. X-ray Diffraction Results

The X-ray diffraction technique is a powerful tool that can provide detailed information about the crystal structure and intermixing of the different materials in a solar cell. In this study, we used XRD analyses to investigate the intermixing between the gig-lox TiO_2 layer and the $\text{CsPbI}_3:\text{EuI}_2$ perovskite material in our solar cell design. XRD analyses revealed that the TiO_2 and perovskite layers had a well-defined crystal structure with distinct diffraction peaks, indicating that the two materials did not undergo any significant phase changes during the fabrication process.

Figure 11 shows the X-ray diffraction patterns of the annealed gig-lox TiO_2 layer infiltrated with $\text{CsPbI}_3:\text{EuI}_2$. The XRD pattern of the bilayer, acquired in the grazing angle (0.8°) configuration, shows the distinctive TiO_2 peaks in the anatase phase at 25.2° and 37.9° [35]. The pattern also bears features of the black orthorhombic γ phase of CsPbI_3 at $2\theta = 14.3^\circ$, 28.6° , 29.1° , 33° , and 36° [35], confirming that the X-ray beam is probing the whole thickness of the bilayer.

The coexistence of distinct crystallographic planes from both the TiO_2 anatase and the γ -phase of $\text{CsPbI}_3:\text{EuI}_2$ provides compelling evidence of their inherent compatibility. This compatibility is of paramount importance as it validates the feasibility of utilizing established processes for the perovskite reaction. The presence of characteristic crystallographic planes signifies a harmonious interaction between the two compounds, creating a favorable environment for the perovskite reaction to occur. This compatibility ensures that the established processes for perovskite deposition and treatment can be seamlessly applied without any detrimental effects on the crystal structure or properties of either compound. The coexistence of crystallographic planes from both TiO_2 anatase and the γ -phase of $\text{CsPbI}_3:\text{EuI}_2$ further implies a synergistic relationship, where the interfacial interaction between the compounds can enhance the performance and stability of the resulting material. This compatibility between the crystal structures opens up new possibilities for optimizing the properties and functionality of perovskite-based devices.

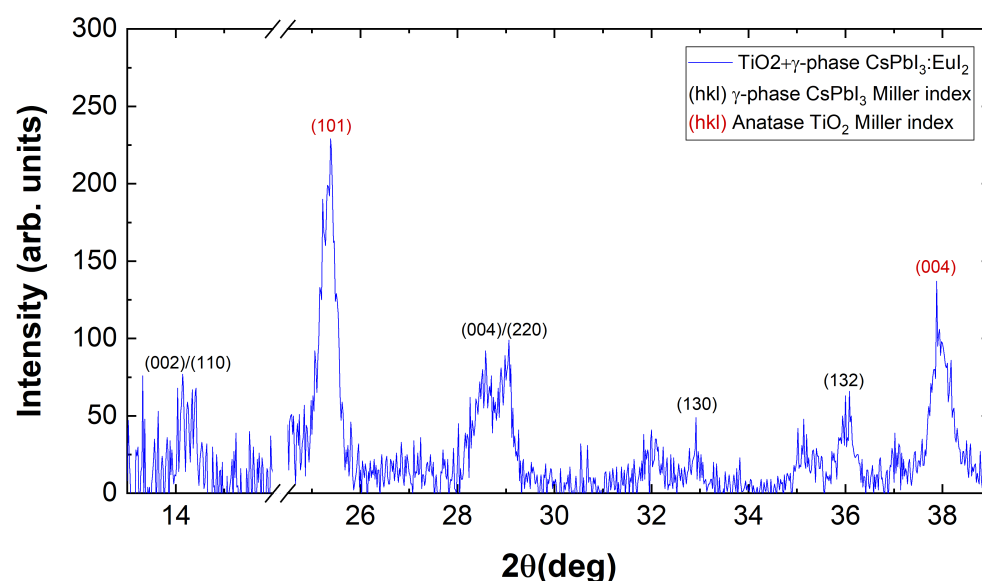


Figure 11. X-ray diffraction patterns of bilayer Gig-Lox $\text{TiO}_2/\text{CsPbI}_3:\text{EuI}_2$.

3.5. Spectroscopic Ellipsometry Results

The determination of optical transmittance holds utmost importance in the pursuit of fabricating high-performance perovskite semi-transparent solar cells [36,37]. This characteristic serves as a distinctive advantage of perovskite solar cells when compared to their silicon counterparts [38]. Understanding and optimizing optical transmittance is crucial in the design and fabrication of perovskite semi-transparent solar cells. The ability of perovskite materials to transmit a significant portion of incident light while efficiently converting it into electricity enables the creation of innovative solar cell architectures with diverse applications [39].

The optical transmittance data, obtained by ellipsometric measurements on the TiO_2 sample with and without infiltrated $\text{CsPbI}_3:\text{EuI}_2$, are shown in Figure 12.

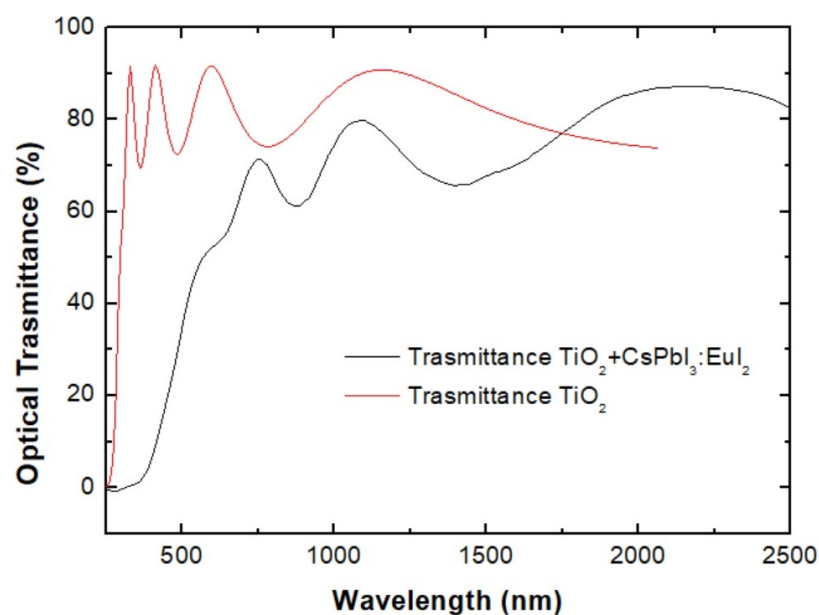


Figure 12. Optical transmittance trend versus wavelength of the annealed gig-lox TiO_2 sample with and without $\text{CsPbI}_3:\text{EuI}_2$ infiltration. The shift in the threshold of the transmittance is an index of the perovskite infiltration. A high transmittance is maintained after perovskite infiltration.

The measured optical transmittance of approximately 75–80% below the bandgap (700 nm) threshold unequivocally demonstrates that the gig-lox TiO_2 film as the ETL layer with $\text{CsPbI}_3:\text{EuI}_2$ does not impede the semi-transparent nature of the final solar cell. These findings reinforce the suitability of perovskite materials for the development of high-performance semi-transparent solar cells, paving the way for their integration into a wide range of innovative applications while advancing the utilization of clean and renewable energy sources [37].

3.6. Photoluminescence Spectroscopy Results

In order to go deeper into the injection of charge carriers from the perovskite to the oxide at the perovskite/ETL interfaces that is well known to impact the device performance, we performed photoluminescence (PL) measurements under nitrogen conditions. The PL measurements were conducted with the perovskite deposited on different substrates: TiO_2 gig-lox, commercial compact TiO_2 (made of nanograins, 20–30 nm in diameter) [40], and bare glass.

Figure 13 displays the emission spectra recorded for:

- $\text{CsPbI}_3:\text{EuI}_2/\text{glass}$;
- $\text{CsPbI}_3:\text{EuI}_2/\text{TiO}_2\text{-compact/glass}$;
- $\text{CsPbI}_3:\text{EuI}_2/\text{TiO}_2\text{-giglox/glass}$.

at different time intervals.

Notably, the perovskite/glass (Figure 13a) and perovskite/ TiO_2 -compact/glass (Figure 13b) samples exhibited the highest PL intensity. On the other hand, the perovskite/ TiO_2 -giglox/glass (Figure 13c) system showed a significant reduction of the recorded PL intensity, indicating an effective charge carrier injection from the perovskite to the ETL [41,42]. This observation is further supported by the fact that, in spite of the higher intensity, the volume of $\text{CsPbI}_3:\text{EuI}_2$ material exposed to light is lower (25%) in the perovskite/glass and perovskite/ TiO_2 -compact/glass systems compared to the perovskite/ TiO_2 -giglox/glass system. All those findings address that the extended interfaces established between the infiltrated perovskite and the TiO_2 sponge are able to boost the injection efficiency of the photogenerated carriers thanks to a spatially distributed built-in potential.

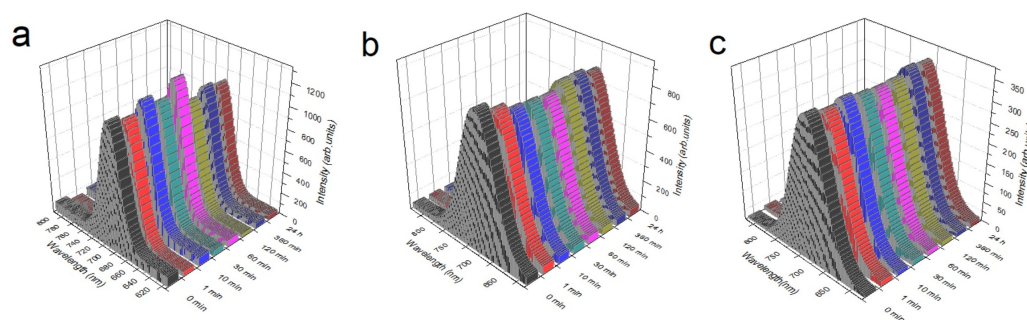


Figure 13. Emission spectra of (a) $\text{CsPbI}_3:\text{EuI}_2/\text{glass}$, (b) $\text{CsPbI}_3:\text{EuI}_2/\text{TiO}_2\text{-compact/glass}$, and (c) $\text{CsPbI}_3:\text{EuI}_2/\text{TiO}_2\text{-giglox/glass}$ recorded at different times.

Additionally, we monitored the stability of the material by collecting the PL signal during the time in a nitrogen atmosphere over a period of 24 h, as depicted in Figure 14. The intensity of the photoluminescence remained stable over time, denoting good stability of the blend, especially for the generation and injection behavior. Finally, we obtain a band gap value of 1.76 eV for the blend. The full width at half maximum value of 40 nm indicated the well-crystallized nature of $\text{CsPbI}_3:\text{EuI}_2$ with minimal defects [43,44]. Moreover, these results underscored the full compatibility and good interface quality between the electron-transporting layer and the perovskite material.

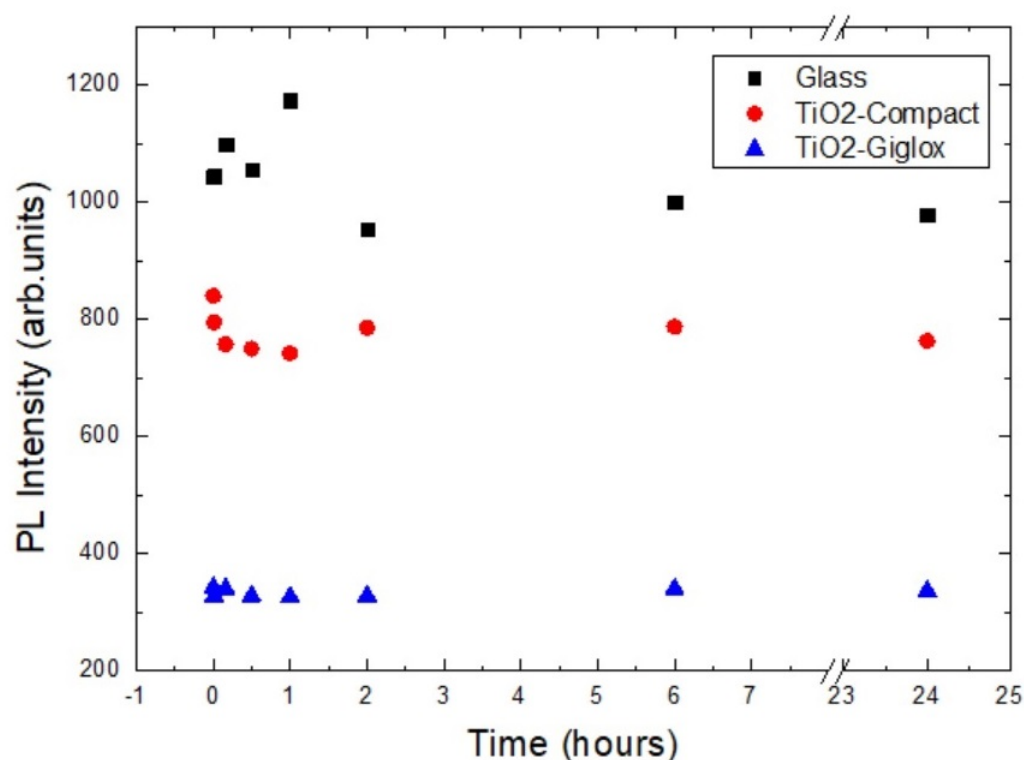


Figure 14. Variation of integrated PL intensity with time.

4. Conclusions

The formation and behavior of a blend material made of a gig-lox TiO_2 layer and an infiltrated perovskite with formulation $\text{CsPbI}_3:\text{EuI}_2$ to be applied as ETL for perovskite solar cells have been studied. We used a gig-lox TiO_2 layer since this material exhibits unique properties, primarily its multi-branched porosity, that allows the perovskite to deeply infiltrate into it.

Moreover, the deposition technique employed for the gig-lox TiO_2 layer (sputtering) is solvent-free and up-scalable, as widely used in the semiconductor industry. The compatibility between the gig-lox TiO_2 layer and the perovskite material was demonstrated by various analyses, including X-ray diffraction and transmission electron microscopy. Photoluminescence was also used as a pivotal practical indicator for the working behavior of the blend under illumination. It provides overall insights into charge carrier generation into the perovskite and injection into the oxide, and indeed on the role of the interfaces. With respect to the behavior of a film of the same perovskite coated on compact TiO_2 , it appears that having more interfaces spread throughout the volume of the blend is advantageous for more effective charge injection and collection by the ETL.

The formation of the TiO_2 -perovskite blend was also shown to be compatible with the perovskite deposition procedure and further treatments, ensuring the transition to the γ -phase of the $\text{CsPbI}_3:\text{EuI}_2$ without altering the oxide layer. The blend material also exhibits good transparency, making it suitable for a wide range of applications, including semi-transparent perovskite solar cells.

The achieved results confirm the effectiveness of spongy gig-lox TiO_2 to work as an electron-transporting layer in perovskite solar cells, opening new perspectives for future research and applications.

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Abbreviations

The following abbreviations are used in this manuscript:

ETL	Electron-transport layer
PSC	Perovskite solar cell
TiO ₂	Titanium dioxide
TEM	Transmission electron microscopy
STEM	Scanning transmission electron microscopy
EDX	Energy-dispersive X-ray analysis
PL	Photoluminescence spectroscopy

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